

## PATENT ABSTRACTS OF JAPAN

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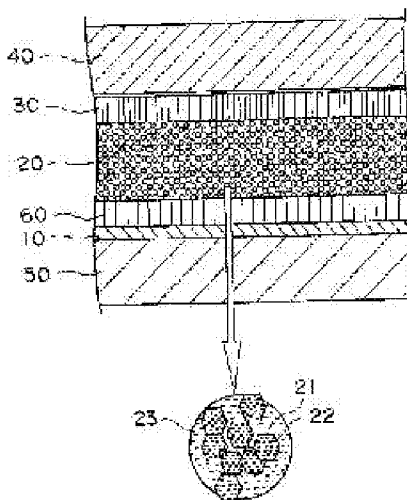
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## (54) PHOTOELECTRIC CONVERSION ELEMENT, MANUFACTURING METHOD OF THE SAME, AND PHOTOCELL

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a photoelectric conversion element using semiconductor fine particle sensitized by pigment, having low cost, practical production aptitude, and excellent conversion efficiency and durability, and to provide a manufacturing method of the same, and a photocell using the same.

SOLUTION: The photoelectric conversion element has a conductive support on which, a semiconductor fine particle containing layer 20 containing semiconductor fine particle to which, pigment is adsorbed, an electric charge transport layer 30, and an opposing electrode 40. The electric charge transport layer 30 is made of gel electrolyte, and the opposing electrode 40 is made of conductive resin. The photocell uses the above photoelectric conversion element. The manufacturing method of the photoelectric conversion element includes an assembling process of sequentially laminating the semiconductor fine particle containing layer, the electric charge transport layer, and the opposing electrode.



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]The anode in which this invention contains spinel type manganic acid lithium as positive active material, It is related with a nonaqueous electrolyte secondary battery provided with the separator which isolates the negative electrodes containing the negative electrode active material in which the insertion and desorption from a lithium ion are possible, and these anodes and negative electrodes, and the gel electrolyte in the armor body, and a manufacturing method for the same.

[0002]

[Description of the Prior Art]In recent years as a cell used for a portable electron, communication equipment, etc., such as a small video camera, a cellular phone, and a notebook computer, An alloy or a carbon material etc. which can be inserted and desorbed from a lithium ion is used as negative electrode active material, Cobalt acid lithium ( $\text{LiCoO}_2$ ), nickel acid lithium ( $\text{LiNiO}_2$ ), the nonaqueous electrolyte secondary battery (lithium secondary battery) represented with the lithium ion battery which uses lithium content multiple oxides, such as manganic acid lithium ( $\text{LiMn}_2\text{O}_4$ ), as a positive electrode material -- a small light weight -- and it also came to be marketed by being put in practical use as a chargeable and dischargeable cell with high capacity.

[0003]A lithium secondary battery with large flexibility of the using form in the apparatus used while recently maintaining the outstanding discharge characteristic came to be required. In particular, it could slim down and there was no liquid leakage, it is lightweight and the small lithium secondary battery excellent in mass energy density came to be demanded. It is in such a background and the lithium secondary battery provided with the polymer electrolyte which made the electrolysis solution gel (hardening), and what is called a lithium polymer secondary battery came to be put in practical use by heating the monomer material of thermal polymerization nature. In the point of this kind of lithium polymer secondary battery having made the electrolysis solution containing a monomer material, and having made this monomer material heat-hardening, it is only that the conventional lithium secondary batteries differ, and battery construction, a manufacturing process, and the material to be used are mostly similar with the conventional lithium secondary battery.

[0004]

[Problem(s) to be Solved by the Invention]It is indispensable to use cyclic carbonate which reduction decomposition cannot be easily carried out within a cell, and polarity is high and is easy to secure ion conductivity as a solvent used for the electrolysis solution for lithium secondary batteries generally. However, cyclic carbonate originates in cyclic structure, and since there is little flexibility and the intermolecular force is strong, it has the fault that viscosity is dramatically strong and cannot \*\*\*\* easily inside an electrode group. For this reason, he is trying to use the mixed solvent which mixed chain (un-annular) carbonate with a weak intermolecular force and small viscosity. Since this chain carbonate does not have polarity higher than cyclic carbonate, ion conductivity is not securable, but it originates in chain structure, and since flexibility is large, it has the strong point in which an intermolecular force is weak and viscosity is small.

[0005]However, in a lithium polymer secondary battery, in order to make a polymeric material contain in an electrolysis solution, the viscosity of the electrolysis solution rose and there was a problem that an electrolysis solution could not \*\*\*\* easily inside an electrode group as compared with a lithium secondary battery. For this reason, it is necessary to make the composition of an electrolysis solution contain many low-boiling point solvent kinds of a chain carbonate system with low viscosity. However, the reduction decomposition of the solvent kind itself was easy to be carried out, and the problem of being easy to generate gas in a cell produced the low-boiling point solvent kind represented by the chain carbonate system.

[0006]It is known that the side reaction for the irreversible efficiency of a battery material (mainly negative pole material) will produce a lithium secondary battery in early stages of charge, and gas will be emitted. In this case, in the lithium secondary battery with which the hard case of an iron can, an aluminium can, etc. is used for the armor body which accommodates a power generation element, it is comparatively hard to produce the problem of starting cell bulging. However, in the lithium polymer secondary battery, since the soft case of the laminate film made from aluminum, etc. was used, the problem of having invited cell bulging with the pressure of the emitted gas, and having an adverse effect on the apparatus to be used was produced.

[0007]In particular, in the lithium polymer secondary battery using manganic acid lithium as positive active material, not only a negative pole material but manganic acid lithium of the positive electrode material participated in disassembly of the electrolysis solution, and had the problem that very a lot of gas was emitted. This is for manganic acid lithium reacting to

strong acid, such as HF which the moisture which exists slightly in an electrolysis solution since it is weak in acid reacted to solutes, such as  $\text{LiPF}_6$ , and produced. For this reason, when manganese dissolves, and dissolved manganese is involved with an electrolysis solution and reacts on a negative electrode out of the crystal of manganic acid lithium, what gas has generated is presumed.

[0008]In this case, since an electrolysis solution has mobility in a lithium secondary battery, even if gas is emitted within a cell, gas does not stagnate in inter-electrode. However, in the lithium polymer secondary battery, since the electrolysis solution was hardened and solidified by gelling, the emitted gas was fixed by inter-electrode and serious problems, such as causing poor charge and discharge, occurred. This is because a what is called "gas \*\*\*\*\*" phenomenon which the gas emitted in the hyperviscous solvent before hardening hardens in the state where it existed in inter-electrode (gelling) arose. For this reason, the portion to which an electrolysis solution (in this case, gelled electrolysis solution) does not exist between an anode and a separator or between a separator and a negative electrode arises. Then, even if it performs charge and discharge after that, it is because a uniform cell reaction could not be performed, poor charge and discharge arose and the battery characteristic fell.

[0009]Then, this invention was made in order to solve the problem mentioned above, and it is \*\*\*\*. Even if it makes the electrolysis solution in which the mixed solvent which is provided with the purpose as positive active material, and contains cyclic carbonate and chain carbonate was made to dissolve a solute gel with the monomer material of thermal polymerization nature (hardening), it is enabling it to provide the nonaqueous electrolyte secondary battery which the heterogeneity of thermal polymerization does not produce.

[0010]

[Means for Solving the Problem]In order to attain the above-mentioned purpose, a nonaqueous electrolyte secondary battery of this invention, It has a separator which isolates an anode which contains spinel type manganic acid lithium as positive active material, negative electrodes containing negative electrode active material in which insertion and desorption from a lithium ion are possible, and these anodes and negative electrodes, and a gel electrolyte in an armor body. And while a gel electrolyte polymerizes in a mixed solvent containing cyclic carbonate and chain carbonate, makes it gel an electrolysis solution in which a solute which consists of lithium salt was dissolved with a monomer material of thermal polymerization nature and formed, A tunic of lithium carbonate in which at least one surface of an anode or a negative electrode was generated by reaction of carbon dioxide and an electrolysis solution which were dissolved in an electrolysis solution is formed.

[0011]Here, carbon dioxide dissolved in an electrolysis solution reacts to a lithium ion in which lithium salt which is a solute of an electrolysis solution dissociated, and forms a minerals tunic of thin lithium carbonate on an anode or a negative electrode surface. Since a tunic of this lithium carbonate coats functional groups [ activity / on a negative electrode ] (-COOH, -NH, -OH, etc.), it can prevent chain carbonate of one solvent from being decomposed by activity functional group. As a result, it becomes possible to obtain a nonaqueous electrolyte secondary battery which can prevent a "gas \*\*\*\*\*" phenomenon from arising at the time of thermal polymerization of a monomer material and with which the heterogeneity of thermal polymerization does not produce it.

[0012]In order that carbon dioxide dissolved in an electrolysis solution may drive out and carry out thermal polymerization of the oxygen dissolved in a polar solvent in an electrolysis solution, etc., uniform thermal polymerization becomes possible and a gel electrolyte (polymer electrolyte) excellent in homogeneity is obtained. Since oxygen configured in a polar solvent in an electrolysis solution was replaced by carbon dioxide whose coordination power is more powerful than oxygen, this is considered. And while a nonaqueous electrolyte secondary battery an energy density, a cycle characteristic, a load characteristic, and whose temperature characteristics improved by having a gel electrolyte (polymer electrolyte) excellent in homogeneity is obtained, A nonaqueous electrolyte secondary battery with which it excelled in safety and generating of gas was controlled at the time of high temperature preservation comes to be obtained.

[0013]In this case, if  $\text{LiPF}_6$  is used as a solute of an electrolysis solution,  $\text{LiPF}_6$  will generate strong acid like HF. Then, HF reacts to chain carbonate weak in acid, and since it decomposes chain carbonate and generates gas, hardening unevenness resulting from "gas \*\*\*\*\*" produces it. However, chain carbonate can be prevented from being decomposed if a minerals tunic of thin lithium carbonate is formed on an anode or a negative electrode surface. If carbon dioxide is made dissolved in an electrolysis solution using  $\text{LiPF}_6$  with high frequency where strong acid like HF is generated especially, as a solute from this, since it will become possible to fully demonstrate an effect of preventing hardening unevenness, it is desirable.

[0014]As spinel type manganic acid lithium used for positive active material, Some manganic acid lithium Magnesium (Mg), boron (B), It is preferred to use spinel type manganic acid lithium replaced or added by at least one sort of elements chosen from fluoride (F), aluminum (aluminum), cobalt (Co), a zirconium (Zr), titanium (Ti), and nickel (nickel).

[0015]As a solvent of an electrolysis solution, it becomes indispensable to use a mixed solvent of cyclic carbonate and chain carbonate. However, although not limited in particular for a solvent kind of cyclic carbonate and chain carbonate, it is preferred to choose from at least one sort of propylene carbonate, ethylene carbonate, and butylene carbonate, and to use as cyclic carbonate. It is preferred to choose from at least one sort of dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate, and to use as chain carbonate.

[0016]It is preferred that end groups, such as polypropylene-glycol diacrylate, use a monomer material which is acrylate especially as a monomer material of thermal polymerization nature. As for polymers which polymerized a monomer material of thermal polymerization nature, it is desirable to use a polyether system solid polymer, a polycarbonate system solid

polymer, a polyacrylonitrile system solid polymer, a copolymer that consists of these two or more sorts, or polymers which constructed the bridge.

[0017]And in order to obtain a nonaqueous electrolyte secondary battery of structure mentioned above, a manufacturing method of a nonaqueous electrolyte secondary battery of this invention, An electrode group accommodation process of accommodating this electrode group in an armor body after making a separator intervening between an anode and a negative electrode and forming an electrode group in it, An electrolysis solution preparation process which dissolves an electrolyte which consists of lithium salt, and a monomer material of thermal polymerization nature in a mixed solvent containing cyclic carbonate and chain carbonate, and prepares an electrolysis solution, A pouring-in process of pouring in an electrolysis solution in atmosphere of carbon dioxide in an armor body in which an electrode group was accommodated, He is trying to have a decompression impregnation process with which an electrode group is impregnated in atmosphere of decompression of an electrolysis solution poured in in an armor body, and a gelling process which gels with heating a monomer material of thermal polymerization nature dissolved in an electrolysis solution, and polymerizes it.

[0018]Thus, when it has a pouring-in process of pouring in an electrolysis solution in atmosphere of carbon dioxide, carbon dioxide comes to be dissolved in an electrolysis solution. By this, in a decompression impregnation process, when an electrode group is impregnated with an electrolysis solution in atmosphere of decompression, a tunic of lithium carbonate will be formed in the surface of an anode, the surface of a negative electrode, or the surface of these two poles. For this reason, in a next curing process, even if it heats and stiffens a monomer material of thermal polymerization nature, hardening unevenness resulting from "gas \*\*\*\*\*" can be prevented from arising.

[0019]In this case, even if it replaces with performing a pouring-in process in atmosphere of carbon dioxide and is made to perform a decompression impregnation process in atmosphere of carbon dioxide, a tunic of lithium carbonate can be formed now at least in one side of two poles, and same effect can be done so. After making it make carbon dioxide dissolved in an electrolysis solution by bubbling etc., even if it pours in this electrolysis solution and makes it impregnate with it beforehand, a tunic of lithium carbonate can be formed now at least in one side of two poles, and same effect can be done so.

[0020]

[Embodiment of the Invention]Subsequently, although an embodiment of the invention is described below based on drawing 1, this invention is not limited to this embodiment at all, and can be suitably carried out in the range which does not change the purpose of this invention. Drawing 1 is a figure showing an example of the nonaqueous electrolyte battery of this invention typically, drawing 1 (a) is a perspective view showing contour shape typically, and drawing 1 (b) is a sectional view showing the A-A section of drawing 1 (a).

[0021]1. The nonaqueous electrolyte secondary battery 10 of nonaqueous electrolyte secondary battery this invention, As shown in drawing 1, it has the electrode group which made the separator 13 which consists of fine porous membrane made from polyethylene intervene between the anode 11 which uses spinel type manganic acid lithium as positive active material, the negative electrodes 12 which use black lead as negative electrode active material, and these two poles. And he is trying to accommodate the electrode group crushed to flat shape in the armor body 14 which consists of an aluminum laminate film. moreover -- the positive electrode lead (not shown) which extended from the anode 11 is connected to the positive pole terminal 15, and the negative electrode lead (not shown) which extended from the negative electrode 12 is connected to the negative pole terminal 16 -- the upper opening of the armor body 14 -- liquid -- it is closed densely.

[0022]It fills up with the gelled electrolysis solution in this armor body 14. As an electrolysis solution, what dissolved  $\text{LiPF}_6$  in the mixed solvent which mixed ethylene carbonate (EC: cyclic carbonate) and diethyl carbonate (DEC: chain carbonate) by the volume ratio of 3:7 at a rate of 1 mol/l as a solute is used. In the electrolysis solution, polypropylene-glycol diacrylate (that whose molecular weight is about 300) as a thermal polymerization nature monomer material, and t-hexyl peroxy pivalate as a polymerization initiator are added (an addition is 5000 ppm). And after being filled up with this electrolysis solution in the armor body 14, it heats at 50 °C for 3 hours, and thermal polymerization of the polypropylene-glycol diacrylate is carried out, and it is made to gel it (hardening).

[0023]Here, there is the important feature of this invention in the tunic of the lithium carbonate generated by the reaction of the carbon dioxide and the electrolysis solution which were dissolved in the above-mentioned electrolysis solution so that it might mention later being formed in the surface of the negative electrode 12, the surface of the anode 11, or the surface of these two poles 11 and 12. If the tunic of lithium carbonate is formed on the surface of the electrode, this tunic will coat functional groups [ activity / on a negative electrode ] (-COOH, -NH, -OH, etc.). For this reason, the solvent of an electrolysis solution can be prevented now from an activity functional group disassembling, and generating of gas can be prevented now. As a result, a "gas \*\*\*\*\*" phenomenon can be prevented from arising at the time of the thermal polymerization of a monomer material, and it comes to carry out thermal polymerization uniformly.

[0024]As positive active material and spinel type manganic acid lithium to be used, Some manganic acid lithium Magnesium (Mg), boron (B), It is desirable to use the spinel type manganic acid lithium replaced or added by at least one sort of elements chosen from fluoride (F), aluminum (aluminum), cobalt (Co), a zirconium (Zr), titanium (Ti), and nickel (nickel). As negative electrode active material, graphite, corks, the tin oxide, metal lithium, silicon, and these mixtures can be used in addition to the black lead mentioned above, and if it is a substance in which the insertion and desorption from a lithium ion are possible, there will be no restriction in particular.

[0025]It is necessary to use the mixed solvent with which cyclic carbonate and chain carbonate were mixed as a solvent of an electrolysis solution. And what is necessary is to choose from at least one sort of propylene carbonate (PC) and butylene carbonate (BC), and just to use as cyclic carbonate, in addition to the ethylene carbonate (EC) mentioned above. What is necessary is to choose from at least one sort of dimethyl carbonate (DMC) and ethyl methyl carbonate, and just to use as

chain carbonate, in addition to the diethyl carbonate (DEC) mentioned above.

[0026] In addition to  $\text{LiPF}_6$  mentioned above as a solute of an electrolysis solution,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ ,  $\text{LiPF}_6 \cdot x(\text{C}_n\text{F}_{2n+1})_x$  (however) It chooses from  $1 \leq x \leq 6$ ,  $n = 1, 2$ , etc., and uses, and these one sort or two sorts or more can be mixed and used. As an addition of lithium salt, 0.2-1.5 mol per l. of electrolysis solution (0.2-1.5 mol/(l.)) is desirable.

[0027] It is preferred that end groups, such as polypropylene-glycol diacrylate, use the monomer material which is acrylate especially as a monomer material of thermal polymerization nature. As for the polymers which polymerized the monomer material of thermal polymerization nature, it is desirable to use a polyether system solid polymer, a polycarbonate system solid polymer, a polyacrylonitrile system solid polymer, the copolymer that consists of these two or more sorts, or the polymers which constructed the bridge. As for the mass ratio of a thermal polymerization nature polymer material and an electrolysis solution, when ion conductivity and the solution retention of an electrolysis solution are taken into consideration, it is desirable to make it become the range of 1:6-1:25. The shape of a cell may be a square shape in addition to the thin shape mentioned above, or may be cylindrical, or what kind of shape may be sufficient as it, and there is no restriction in particular also about the size.

[0028] 2. Explain below the production procedures of the nonaqueous electrolyte secondary battery 10 of a nonaqueous electrolyte secondary battery produced thus constituted in detail. [Drawing 2](#) shows the outline of the process procedure for producing the nonaqueous electrolyte secondary battery 10 of this invention. In [drawing 2](#), the nonaqueous electrolyte secondary battery 10 of this invention performs the drying process which dries an electrode group, after performing the coiling stage which the separator 13 is made to intervene among these two poles 11 and 12, is wound, and is made into an electrode group after performing first the electrode making process which produces the anode 11 and the negative electrode 12. Subsequently, the armor body which accommodated the electrode group is arranged in a dry box. Then, the pouring-in process of pouring in an electrolysis solution in an armor body, the impregnation process with which it impregnates in an electrode group in the atmosphere of decompression of the poured-in electrolysis solution, and the temporary sealing process which carries out temporary closure of the opening of an armor body are performed in a dry box.

[0029] Subsequently, after gelling the thermal polymerization nature monomer material which heats the armor body by which temporary closure was carried out, and exists in an electrolysis solution and making it heat-harden, heat curing and the aging process to age are performed. It becomes a completion cell at the last through this sealing process which carries out actual closure of the armor body. In this invention, the method of performing a pouring-in process in the atmosphere of carbon dioxide, the method of performing an impregnation process in the atmosphere of carbon dioxide, and the method of making it beforehand dissolved in an electrolysis solution by bubbling etc. are adopted as a means to make carbon dioxide dissolved in an electrolysis solution. Although some concrete examples of the nonaqueous electrolyte battery of this invention are described below, in order to clarify the effect of this invention, various comparative examples are also explained collectively.

[0030] (1) Some manganese as example 1 positive active material is replaced by magnesium (Mg), And the graphite powder as a carbon conducting agent was mixed with the spinel type manganic acid lithium ( $\text{Li}_{1.06}\text{Mn}_{1.88}\text{Mg}_{0.04}\text{O}_4\text{B}_{0.01}$ ) in which boron (B) was added (it is 92:5 at a mass ratio), and it was considered as positive electrode mixture powder. Subsequently, it was filled up with the obtained positive electrode mixture powder in the mixed device (for example, Hosokawa Micron mechano fusion device (AM-15F)). Operated this for 10 minutes at per minute 1500 times of number of rotations (1500 rpm), compression, the shock, and the shearing action were made to cause, and it mixed.

[0031] Then, the fluoro-resin system binder was mixed at a fixed rate (it is 97:3 at a mass ratio), and it was considered as positive electrode mixture. Subsequently, both sides of the positive pole collector which consists of aluminum foil were plastered with this positive electrode mixture, after drying, it rolled in predetermined thickness, it cut in predetermined shape, and the anode 11 was produced. It may mix by a slurry regime, using positive electrode mixture powder as it is, without facing mixing positive electrode mixture powder and using a mechano fusion device. It may be made to mix by other methods.

[0032] On the other hand, in the size (Lc) of the microcrystal of c shaft orientations, the spacing ( $d_{002}$ ) of the field used the powder of massive black lead (artificial graphite calcinated at 2950 \*\*) whose mean particle diameter is 20 micrometers in 200 nm at 0.336 nm as negative electrode active material (002). This graphite powder and a styrene system binder were mixed at a fixed rate (it is 98:2 at a mass ratio), and water was added to this, and it mixed to it, and was considered as negative electrode mixture. Then, both sides of the negative pole collector which consists of copper foil were plastered with this negative electrode mixture, after drying, it rolled in predetermined thickness, it cut in predetermined shape, and the negative electrode 12 was produced.

[0033] 1 mol/l. of lithium hexafluoride phosphorate ( $\text{LiPF}_6$ ) was dissolved in the mixed solvent which mixed ethylene carbonate (EC) and diethyl carbonate (DEC) by the volume ratio of 3:7, and the electrolysis solution ( $\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$ ) was prepared. Subsequently, while adding polypropylene-glycol diacrylate (that whose molecular weight is about 300) as a monomer material of thermal polymerization nature to this electrolysis solution so that a mass ratio with an electrolysis solution may be set to 15:1, 5000 ppm of t-hexyl peroxy pivalate was added as a polymerization initiator, and the mixed electrolysis solution was produced. As for the addition of the monomer material added to an electrolysis solution, when the point of ion conductivity or liquid holdout is taken into consideration, it is desirable to add so that the mass ratio to an electrolysis solution may become the range of 6:1-25:1.

[0034] Subsequently, the separator 13 which consists of fine porous membrane made from polyethylene among these was made to intervene using the anode 11 and the negative electrode 12 which were produced as mentioned above, and it piled up, and wound spirally. Subsequently, this was crushed so that it might become flat, the electrode group of flat shape was

produced, and the back carried out predetermined time desiccation of this electrode group. Subsequently, after accommodating an electrode group in the armor body 14 which consists of an aluminum laminate film, this has been arranged in a dry box. Then, the inside of a dry box was made into the atmosphere of carbon dioxide, and the electrolysis solution produced as mentioned above was poured in in the armor body 14. By this, carbon dioxide will be dissolved in an electrolysis solution.

[0035]subsequently, it was alike in if the inside of a dry box is replaced by nitrogen gas or argon gas and the inside of a dry box is made into the atmosphere of nitrogen gas or argon gas, the inside of a dry box was attracted with the vacuum pump, and it was made the atmosphere of decompression. The electrolysis solution poured in in the armor body 14 will be impregnated in an electrode group by this, and the tunic of lithium carbonate will be formed in the surface of the anode 11, the surface of the negative electrode 12, or the surface of these two poles 11 and 12. Then, temporary closure of the opening of the armor body 14 was carried out, and it took out from the dry box. Subsequently, after having arranged this in heating apparatus, the inside of heating apparatus was held in temperature of 50 \*\*, and was heated for 3 hours. Polypropylene-glycol diacrylate which is a monomer material of thermal polymerization nature will polymerize by this, and an electrolysis solution will be hardened by gelling. Subsequently, design capacity produced the nonaqueous electrolyte battery A of Example 1 of 600mAh by carrying out actual closure of the opening of the armor body 14.

[0036](2) To the mixed solvent mixed by the volume ratio of 3:7, example 2 ethylene carbonate (EC) and diethyl carbonate (DEC). Except having dissolved 1 mol/l. of lithiumimide salt ( $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ ), and having prepared the electrolysis solution ( $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2/\text{EC}:\text{DEC}=3:7$ ), The nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery B of Example 2.

[0037](3) To the mixed solvent mixed by the volume ratio of 3:7, example 3 ethylene carbonate (EC) and diethyl carbonate (DEC). 0.5 mol/l. of lithium hexafluoride phosphorate. ( $\text{LiPF}_6$ ) and 0.5 mol/l. of lithiumimide salt. Except having dissolved ( $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ ) and having prepared the electrolysis solution ( $\text{LiPF}_6+\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2/\text{EC}:\text{DEC}=3:7$ ), The nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery C of Example 3.

[0038](4) Except having used the mixed positive active material which mixed spinel type manganic acid lithium ( $\text{Li}_{1.06}\text{Mn}_{1.88}\text{Mg}_{0.04}\text{O}_4\text{B}_{0.01}$ ) and cobalt acid lithium (it is 1:1 at a mass ratio) as example 4 positive active material, After preparing an electrolysis solution ( $\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$ ) like Example 1 mentioned above, the nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery D of Example 4.

[0039](5) After accommodating the electrode group produced like example 5 Example 1 in the armor body 14 and arranging in a dry box, the inside of a dry box is made into the atmosphere of nitrogen gas or argon gas, The same electrolysis solution ( $\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$ ) as Example 1 mentioned above was poured in in the armor body 14. subsequently, it was alike in if the inside of a dry box is replaced by carbon dioxide and the inside of a dry box is made into the atmosphere of carbon dioxide, the inside of a dry box was attracted with the vacuum pump, and it was made the atmosphere of decompression. The electrolysis solution poured in in the armor body 14 will be impregnated in an electrode group by this, carbon dioxide will be dissolved in an electrolysis solution, and the tunic of lithium carbonate will be formed in the surface of the anode 11, the surface of the negative electrode 12, or the surface of these two poles 11 and 12. Subsequently, the nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery E of Example 5.

[0040](6) After preparing an electrolysis solution ( $\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$ ) like Example 1 mentioned above example 6, the polymeric material and the polymerization initiator were added like Example 1 mentioned above, and it was considered as the mixed electrolysis solution. You made it dissolved by what carbon dioxide is blown into this for under room temperature ordinary pressure (bubbling) until carbon dioxide was saturated in an electrolysis solution. Subsequently, after accommodating the electrode group produced like Example 1 in the armor body 14 and having arranged this in a dry box, the inside of a dry box was made into the atmosphere of nitrogen gas or argon gas, and the electrolysis solution in which this carbon dioxide was dissolved was poured in in the armor body 14. By this, the tunic of lithium carbonate will be formed in the surface of the anode 11, the surface of the negative electrode 12, or the surface of these two poles 11 and 12. Subsequently, the inside of the dry box of the atmosphere of nitrogen gas or argon gas was made decompression, and after being impregnated with the electrolysis solution poured in in the armor body 14 in the electrode group, it produced the nonaqueous electrolyte battery like Example 1 mentioned above, and made this the nonaqueous electrolyte battery F of Example 6.

[0041](7) The pouring-in process and impregnation process of the electrolysis solution ( $\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$ ) prepared like Example 1 mentioned above are performed in the atmosphere of nitrogen gas or argon gas, using cobalt acid lithium as comparative example 1 positive active material, Except not having made carbon dioxide dissolved in an electrolysis solution, the nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery R of the comparative example 1.

[0042](8) Except having used cobalt acid lithium as comparative example 2 positive active material, after preparing an electrolysis solution ( $\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$ ) like Example 1 mentioned above, the nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery S of the comparative example 2.

[0043](9) Ethylene carbonate (EC: cyclic carbonate) and propylene carbonate (PC: cyclic carbonate) to the mixed solvent mixed by the volume ratio of 3:7, using cobalt acid lithium as comparative example 3 positive active material. 1 mol/l. of lithium hexafluoride phosphorate ( $\text{LiPF}_6$ ) was dissolved, and the electrolysis solution ( $\text{LiPF}_6/\text{EC}:\text{PC}=3:7$ ) was prepared, And

the pouring-in process and impregnation process of this electrolysis solution were performed in the atmosphere of nitrogen gas or argon gas, except not having made carbon dioxide dissolved in an electrolysis solution, the nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery T of the comparative example 3.

[0044](10) The pouring-in process and impregnation process of the electrolysis solution ( $\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$ ) prepared like comparative example 4 Example 1 are performed in the atmosphere of nitrogen gas or argon gas, Except not having made carbon dioxide dissolved in an electrolysis solution, the nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery U of the comparative example 4.

[0045](11) The electrolysis solution ( $\text{LiPF}_6/\text{EC}+\text{PC}$ ) prepared like the comparative example 5 comparative example 3 is used, And the pouring-in process and impregnation process of this electrolysis solution beta 4 were performed in the atmosphere of nitrogen gas or argon gas, except not having made carbon dioxide dissolved in the electrolysis solution beta 4, the nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery V of the comparative example 5.

[0046](12) The electrolysis solution ( $\text{Li}(\text{SO}_2\text{C}_2\text{F}_5)_2/\text{EC}:\text{DEC}=3:7$ ) prepared like comparative example 6 Example 2 is used, And the pouring-in process and impregnation process of this electrolysis solution were performed in the atmosphere of nitrogen gas or argon gas, except not having made carbon dioxide dissolved in an electrolysis solution, the nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery W of the comparative example 6.

[0047](13) Polyvinylidene fluoride (PVdF) is used as comparative example 7 polymeric material, And the pouring-in process and impregnation process of the electrolysis solution ( $\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$ ) prepared like Example 1 are performed in the atmosphere of nitrogen gas or argon gas, Except not having made carbon dioxide dissolved in an electrolysis solution, the nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery X of the comparative example 7. Although polyvinylidene fluoride (PVdF) is already polymers-ized, Although there are two kinds, the type gelled because this absorbs liquid and swells, and the type which fuses with an electrolysis solution at an elevated temperature, and incorporates an electrolysis solution all over a polymer network by cooling, the latter thing is used in this example.

[0048](14) Except having used polyvinylidene fluoride (PVdF) as comparative example 8 polymeric material, Using the electrolysis solution ( $\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$ ) prepared like Example 1 mentioned above, the nonaqueous electrolyte battery was produced like Example 1, and this was made into the nonaqueous electrolyte battery Y of the comparative example 8. About polyvinylidene fluoride (PVdF), the thing of a type which incorporates an electrolysis solution all over a polymer network is used by fusing with an electrolysis solution and cooling at the same elevated temperature as \*\*\*\*.

[0049](15) The same positive active material ( $\text{Li}_{1.06}\text{Mn}_{1.88}\text{Mg}_{0.04}\text{O}_4\text{B}_{0.01}+$  cobalt acid lithium) as comparative example 9 Example 4 is used, The pouring-in process and impregnation process of the electrolysis solution ( $\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$ ) prepared like Example 1 are performed in the atmosphere of nitrogen gas or argon gas, Except not having made carbon dioxide dissolved in an electrolysis solution, the nonaqueous electrolyte battery was produced like Example 1 mentioned above, and this was made into the nonaqueous electrolyte battery Z of the comparative example 9.

[0050]3. The charge and discharge test occasion and the design capacity produced as mentioned above each of these cells using cell A-F of Examples 1-6 of 600mAh, and cell R-Z of the comparative examples 1-9 at a room temperature (about 25 \*\*). It charged with the constant voltage after charging by constant current until cell voltage was set to 4.2V by 600-mA charging current until the current value was set to 30 mA or less after reaching 4.2V. Subsequently, after stopping at a room temperature (about 25 \*\*) for 10 minutes, when were a room temperature (about 25 \*\*), and it was made to discharge until cell voltage was set to 2.75V by 600-mA discharge current and early service capacity was calculated from the charging time value this time, the result as shown in the following table 1 was obtained.

[0051]When each of these cells were disassembled, the surface state of the negative electrode 12 was observed and the hardening unevenness of the negative electrode surface was checked by viewing after charge, the result as shown in the following table 1 was obtained. It carried out by repeating the charge cycle which makes above-mentioned charge and discharge one cycle using the cell A of Example 1, and the cell U of the comparative example 4. And when the service capacity for every cycle was calculated and having been asked for the ratio of the calculated service capacity and initial service capacity, the result as shown in drawing 4 was obtained. In the negative-electrode hardening unevenness of Table 1, it is shown that hardening unevenness had generated so much what attached \* seal for "being."

[0052]

[Table 1]

電池 種類	正極活物質	電解液 (リチウム塩/溶媒)	炭酸ガス の溶解時	ポリマ ー	放電容 量 mAh	負極硬 化の有
A	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$	$\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$	注液時	熱重合	603	なし
B	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$	$\text{LiN}(\text{SO}_2\text{CF}_3)_2$ / $\text{EC}:\text{DEC}=3:7$	注液時	熱重合	600	なし
C	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$	$\text{LiPF}_6+\text{LiN}(\text{SO}_2\text{CF}_3)_2$ / $\text{EC}:\text{DEC}=3:7$	注液時	熱重合	601	なし
D	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$ +コバール酸リチウム	$\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$	注液時	熱重合	599	なし
E	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$	$\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$	充電時	熱重合	601	なし
F	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$	$\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$	電解液中	熱重合	602	なし
R	コバール酸リチウム	$\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$	なし	熱重合	601	なし
S	コバール酸リチウム	$\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$	注液時	熱重合	599	なし
T	コバール酸リチウム	$\text{LiPF}_6/\text{EC}:\text{PC}=3:7$	なし	熱重合	554	有り
U	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$	$\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$	なし	熱重合	571	有り*
V	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$	$\text{LiPF}_6/\text{EC}:\text{PC}=3:7$	なし	熱重合	527	有り*
W	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$	$\text{LiN}(\text{SO}_2\text{CF}_3)_2$ / $\text{EC}:\text{DEC}=3:7$	なし	熱重合	584	有り
X	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$	$\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$	なし	PVdF	601	なし
Y	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$	$\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$	注液時	PVdF	601	なし
Z	$\text{Li}_1.0\text{Mn}_1.0\text{Mg}_{0.0}\text{Co}_{0.0}\text{O}_{0.0}$ +コバール酸リチウム	$\text{LiPF}_6/\text{EC}:\text{DEC}=3:7$	なし	熱重合	583	有り

[0053]4. Cell R of comparative example 1 which is not dissolved in carbon dioxide in electrolysis solution using effect cobalt acid lithium of carbon dioxide \*\*\*\* at the time of using examination (1) cobalt acid lithium of test result as positive active material as positive active material. When the cell S of the comparative example 2 dissolved in carbon dioxide in the electrolysis solution is compared, it turns out that the difference has produced only the error (for example, mass error at time of mixture spreading, etc.) grade on cell production to the design capacity of 600mAh in neither of the cells. This is not concerned with the existence of \*\*\*\* of the carbon dioxide in an electrolysis solution, is not concerned with whether the coat of lithium carbonate is formed in the electrode surface, but shows that battery capacity is fully pulled out. In the disassembled negative electrode, it turned out that polymer is also hardened uniformly and is charged uniformly.

[0054]Although the moisture which exists slightly in an electrolysis solution reacts to lithium salt, such as  $\text{LiPF}_6$ , acid, such as HF, is generated, and this reacts to positive active material and promotes disassembly of an electrolysis solution, this, To acid, since it is not so sensitive, cobalt acid lithium is considered for not promoting disassembly of an electrolysis solution. From these things, when cobalt acid lithium is used as positive active material, it can be said that the effect of making the coat of lithium carbonate forming in an electrode surface is not demonstrated even if it makes carbon dioxide dissolved in an electrolysis solution.

[0055](2) The cell R of the comparative example 1 using [ using necessity cobalt acid lithium of a low-boiling point solvent kind (chain carbonate system solvent) as positive active material ] the mixed solvent (EC+DEC) of cyclic carbonate and chain carbonate. When the cell T of the comparative example 3 using the mixed solvent (EC+PC) of cyclic carbonate is compared, it turns out that the early service capacity of the cell T is low 47 mAh from the cell R. The cell U of the comparative example 4 using [ using manganic acid lithium as positive active material ] the mixed solvent (EC+DEC) of cyclic carbonate and chain carbonate. When the cell V of the comparative example 5 using the mixed solvent (EC+PC) of cyclic carbonate is compared, it turns out that the early service capacity of the cell V is low 44 mAh from the cell U.

[0056]Since polarity of cyclic carbonate is strong, ion conductivity is excellent, but on the structure of being annular, since this has little flexibility, the tendency for an intermolecular force to become high is strong, and viscosity is dramatically high. For this reason, in the cell T of the comparative example 3 using the mixed solvent (EC+PC) of cyclic carbonate, and the cell V of the comparative example 5, it is difficult to make an electrolysis solution fully permeate in the electrode (the anode 11 and the negative electrode 12) with which it high-filled up, and it is thought that a result to which initial service capacity fell was brought. In order to carry out that it is easy to make an electrolysis solution permeate in an electrode, it is effective in a cell to add a surface-active agent, but it does not have an adverse effect on battery capacity, or since the surface-active agent itself is not preferred environmentally, it cannot be said that it is an effective means.

[0057]On the other hand, since chain carbonate does not have polarity as high as cyclic carbonate, there are few conductive auxiliary effects, but on the structure of a chain, since flexibility is large, an intermolecular force is small, and viscosity is low. For this reason, in the cell R of the comparative example 1 using the mixed solvent (EC+DEC) of cyclic carbonate and chain carbonate, and the cell U of the comparative example 4, An electrolysis solution can be made to fully permeate in the electrode (the anode 11 and the negative electrode 12) with which it high-filled up now, and it is thought that the fall of initial



service capacity has been controlled. However, since the inside of a cell immediately after electrolysis solution pouring in has dramatically high reduction nature, it is decomposed easily and chain carbonate which is easy to be returned generates gas.

[0058]when cobalt acid lithium is used as positive active material, as mentioned above, the generation of gas is not produced, but when manganic acid lithium is used as positive active material, since this generates gas, it is serious -- a problem -- \*\* This is for the moisture which exists slightly in an electrolysis solution reacting to lithium salt, such as  $\text{LiPF}_6$ , and generating acid, such as HF, and this reacting to manganic acid lithium of positive active material, and promoting disassembly of an electrolysis solution. For this reason, in the cell U of the comparative example 4 using the mixed solvent (EC+DEC) of cyclic carbonate and chain carbonate, initial service capacity is considered to have brought a result to which only 29 mAh fell rather than design capacity, using manganic acid lithium as positive active material.

[0059]The following matters become clear from these things. That is, in the nonaqueous electrolyte battery which carried out thermal polymerization within the cell and gelled the electrolysis solution, it becomes indispensable to use the mixed solvent of cyclic carbonate and chain carbonate. However, when manganic acid lithium is used for positive active material, chain carbonate is decomposed, gas is generated and service capacity falls. For this reason, it is necessary to control decomposition of chain carbonate. Then, the effect of this invention is examined in detail below.

[0060](3) pouring in an electrolysis solution in the atmosphere of effect \*\*\*\* of carbon dioxide \*\*\*\* at the time of using manganic acid lithium as positive active material, nitrogen gas, or argon gas, and with the cell U of the comparative example 4 by which carbon dioxide is not dissolved in the electrolysis solution. An electrolysis solution is poured in in the atmosphere of carbon dioxide, and the cell A of Example 1 which made carbon dioxide dissolved in an electrolysis solution is compared. It turns out that initial service capacity is falling [ 29 mAh ] to design capacity in the cell U of the comparative example 4 which poured in the electrolysis solution in the atmosphere of nitrogen gas or argon gas. In the cell U of the comparative example 4, as shown in [drawing 3](#), it turned out that the hardening unevenness 12a which originates everywhere in the negative electrode 12 at "gas \*\*\*\*\*" has occurred.

[0061] $\text{LiPF}_6$  used as a solute reacts to the moisture which exists slightly in an electrolysis solution, and this generates strong acid, such as HF. Then, manganic acid lithium especially sensitive to acid reacts to the acid by which it was generated, and manganese ion is made eluted in an electrolysis solution. this eluted manganese ion should be involved the active functional group and electrolysis solutions with which it is dotted on a negative electrode surface, such as  $-\text{COOH}$ ,  $-\text{NH}$ , and  $-\text{OH}$ , -- it \*\*\*\*\* and a lot of gas is generated. And since the monomer material of thermal polymerization nature exists in an electrolysis solution, it is in the state where viscosity is high. For this reason, the emitted gas will stagnate in inter-electrode, a monomer will carry out thermal polymerization in this state, and an electrolysis solution will be gelled. As a result, it will be in the state where it does not fully fill up with an electrolysis solution between the anode 11-separator 13-negative electrodes 12, and it will be thought that initial service capacity fell.

[0062]On the other hand, the electrolysis solution was poured in in the atmosphere of carbon dioxide, and the initial service capacity as design capacity was mostly obtained in the cell A of Example 1 which made carbon dioxide dissolved in an electrolysis solution. Generating of the hardening unevenness 12a resulting from "gas \*\*\*\*\*" as shown in [drawing 3](#) was not accepted, either, and it became what was charged uniformly. For the moment, the reason which brought such a result can be guessed as follows, although it cannot fully grasp. That is, the carbon dioxide dissolved in the electrolysis solution reacts to the lithium ion ( $\text{Li}^+$ ) in which lithium salt of  $\text{LiPF}_6$  which is a solute dissociated, and forms the minerals coat of thin lithium carbonate in the surface of the anode 11, or the surface of the negative electrode 12. Then, this coat is wrapped in so that active functional groups, such as  $-\text{COOH}$  with which it is dotted on a negative electrode surface,  $-\text{NH}$ , and  $-\text{OH}$ , may be coated, advance of a side reaction like [ at the time of not making carbon dioxide dissolved ] is checked, and it is thought that generating of the hardening unevenness 12a resulting from "gas \*\*\*\*\*" has been controlled.

[0063]Here, since the portion of the hardening unevenness 12a is in the state where an electrolysis solution does not exist easily when the hardening unevenness 12a resulting from "gas \*\*\*\*\*" is formed, as shown in [drawing 3](#), lithium deposits easily around this hardening unevenness 12a. And the side reaction of the depositing lithium is carried out to an electrolysis solution, it generates gas, it checks a regular charge-and-discharge reaction, and poor charge and discharge generate it. And if a charging and discharging cycle is repeated in this state, the part where charge and discharge are poor will be expanded, and rapid degradation will be caused into a charging and discharging cycle. Since depositing lithium causes an abnormal heat generation at the temperature near 100 \*\*, it may cause abnormalities, such as internal combustion.

[0064]It can be said that the result of [drawing 4](#) shows this clearly. That is, in the cell U of the comparative example 4 by which the curing failure of polymer is accepted, with progress of a charging and discharging cycle, the part where charge and discharge are poor was expanded, and the cycle characteristic has deteriorated rapidly. On the other hand, in the cell A of Example 1 by which curing failure is not accepted, since it has polymerized uniformly, an unusual reaction does not arise, but the action of monotonous cycle characteristic degradation is carried out. It can be said that it becomes a means very effective when securing the uniform polymerization nature of polymer from this to make carbon dioxide dissolved in an electrolysis solution when manganic acid lithium is used as positive active material.

[0065](4) The cell U of the comparative example 4 which makes effect  $\text{LiPF}_6$  of carbon dioxide \*\*\*\* at the time of using  $\text{LiPF}_6$  as lithium salt the solute of an electrolysis solution. When the cell W of the comparative example 6 which makes  $\text{Li}(\text{SO}_2\text{C}_2\text{F}_5)_2$  the solute of an electrolysis solution is compared, it turns out that the direction of the cell W has high initial service capacity. As for this, since  $\text{Li}(\text{SO}_2\text{C}_2\text{F}_5)_2$  eased generating of the hardening unevenness 12a which originates in "gas \*\*\*\*\*" like the cell U of the comparative example 4 since strong acid like HF is not generated like  $\text{LiPF}_6$ , it is considered.

However, the cell B of Example 2 which made  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$  carbon dioxide dissolved in an electrolysis solution using the solute of an electrolysis solution. And when the cell C of Example 3 and the cell W of the comparative example 6 which made carbon dioxide dissolved in an electrolysis solution using the mixed solute of  $\text{LiPF}_6$  and  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$  are compared, it turns out that the direction of the cells B and C has high initial service capacity.

[0066]Although  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$  does not generate strong acid like HF like  $\text{LiPF}_6$ , generating acid weaker than HF is known, decomposition of chain carbonate takes place with this weak acid, and this generates gas. For this reason, in the cell W, the hardening unevenness 12a resulting from "gas \*\*\*\*\*" is generated, and it is thought that initial service capacity fell. On the other hand, in the cells B and C, generating of the hardening unevenness 12a which originates in "gas \*\*\*\*\*" for the reason mentioned above is prevented, and it is thought that initial service capacity did not fall. If carbon dioxide is made dissolved in the electrolysis solution using  $\text{LiPF}_6$  with high frequency where strong acid like HF is generated especially, as a solute from this, it becomes possible to fully demonstrate the effect of preventing hardening unevenness, and it can be said that it is effective.

[0067](5) In the cell X of the comparative example 7 and the cell Y of the comparative example 8 using PVdF as a necessity polymeric material of a thermal polymerization nature polymer material, it turns out that the difference has produced only the error grade on cell production to the design capacity of 600mAh in neither of the cells. Carbon dioxide is dissolved in an electrolysis solution, or this is not concerned with no, is not concerned with whether the coat of lithium carbonate is formed in the electrode surface, but shows that battery capacity is fully pulled out. In the disassembled negative electrode, it turned out that polymer is also hardened uniformly and is charged uniformly.

[0068]Since PVdF is not a polymer material of thermal polymerization nature, if PVdF is added in an electrolysis solution, as for this, the viscosity of an electrolysis solution will rise. However, since mobility is maintained even if viscosity rises, even if gas is emitted in process of gelling, by the time it gels the emitted gas thoroughly, it will come to escape from and come out of inter-electrode, without stopping at inter-electrode. For this reason, even if carbon dioxide is not dissolved in the electrolysis solution, and dissolved, it is thought that same result was brought. In order to demonstrate from this the effect of making carbon dioxide dissolved in an electrolysis solution, when the monomer material of thermal polymerization nature is used, it can be said that it is effective. As a monomer material of thermal polymerization nature, that whose end group is acrylate is preferred.

[0069](6). Used the mixed positive active material (it is 1:1 at a mass ratio) which mixed cobalt acid lithium for effect manganic acid lithium of carbon dioxide \*\*\*\*\* at the time of using for manganic acid lithium the mixed positive active material which mixed cobalt acid lithium. When the cell D of Example 4 is compared with the cell Z of the comparative example 9, as for initial service capacity, it turns out that the direction of 16 mAh of the cell D is improving also in the cell Z twist. Since the effect of making carbon dioxide dissolved in an electrolysis solution in order that this manganic acid lithium may participate in disassembly of an electrolysis solution, if the manganic acid lithium which reacts sensitively to acid content into an anode contains was demonstrated, this is considered. As for the content of manganic acid lithium, since the effect in which carbon dioxide is made dissolved cannot be demonstrated if there is too little content of manganic acid lithium, it is desirable that more than 10 mass % uses more than 30 mass % preferably to the mass of mixed positive active material.

[0070](7) The cell A of Example 1 with which it was impregnated in the atmosphere of nitrogen gas or argon gas after pouring in the difference pan of the dissolved method into the electrolysis solution of carbon dioxide in the atmosphere of carbon dioxide. The cell E of Example 5 with which it was impregnated in the atmosphere of carbon dioxide after pouring in in the atmosphere of nitrogen gas or argon gas. When the cell F of Example 6 which poured in the electrolysis solution in which carbon dioxide was made dissolved beforehand in the atmosphere of nitrogen gas or argon gas and with which it was impregnated is compared, it turns out that the difference has produced only the error grade on cell production to the design capacity of 600mAh in neither of the cells. there is this about carbon dioxide at the time of pouring in -- it is -- the time of being impregnated -- or even if you make it beforehand dissolved in an electrolysis solution, the introductory effect of carbon dioxide can be done so by any methods.

[0071]

[Effect of the Invention]The anode which contains spinel type manganic acid lithium as positive active material in this invention as mentioned above, The heterogeneity of the polymerization by the generating gas which had become a pending matter in the combination of the electrolysis solution which consists of the mixed solvent and solute of cyclic carbonate and chain carbonate, and a thermal polymerization nature monomer is improved by making carbon dioxide dissolved in an electrolysis solution. As a result, the nonaqueous electrolyte battery which has the outstanding battery capacity can be provided now.

[0072]In this invention, in order that the carbon dioxide dissolved in the electrolysis solution may drive out and carry out thermal polymerization of the oxygen dissolved in the polar solvent in an electrolysis solution, etc., uniform thermal polymerization becomes possible and the polymer electrolyte excellent in homogeneity is obtained. Since the oxygen configured in the polar solvent in an electrolysis solution was replaced by the carbon dioxide whose coordination power is more powerful than oxygen, this is considered. And while the nonaqueous electrolyte secondary battery an energy density, a cycle characteristic, a load characteristic, and whose temperature characteristics improved by having the polymer electrolyte excellent in homogeneity is obtained, the nonaqueous electrolyte secondary battery with which it excelled in safety and the generation of gas decreased at the time of high temperature preservation comes to be obtained.

[Translation done.]

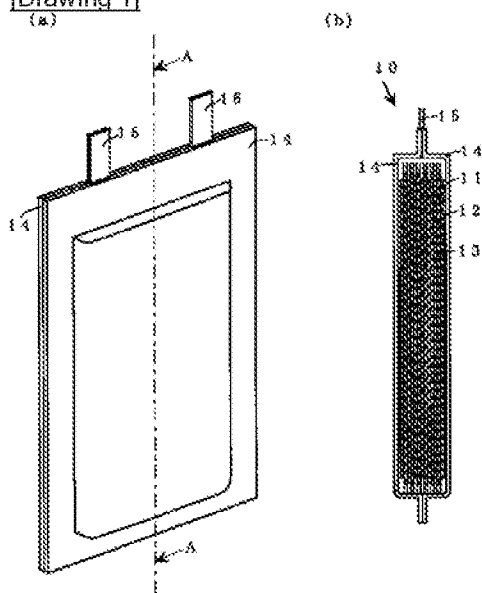
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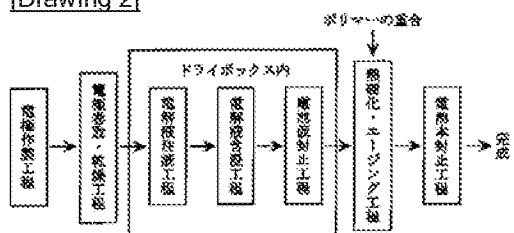
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

## DRAWINGS

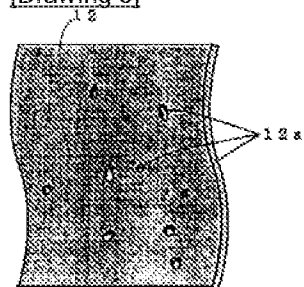
[Drawing 1]



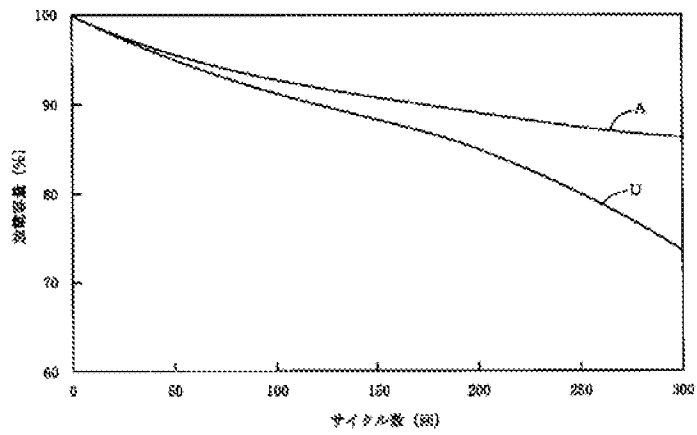
[Drawing 2]



[Drawing 3]



[Drawing 4]



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[Translation done.]